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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Yasushi Kurata, et al

Serial No.: 10/049,672

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For: POLISHING MEDIUM FOR CHEMICAL-MECHANICAL
POLISHING, AND METHOD OF POLISHING SUBSTRATE
MEMBER

Art Unit: 1765

Examiner: Deo, DUY VU NGUYEN

DECLARATION UNDER 37 CFR 1.132

Commissioner For Patents
Washington, D.C. 20231

Sir:

I, Yasushi Kurata, Japanese citizen, High Performance Materials R&D Center Hitachi Chemical Co., Ltd., Yamazaki Works (Katsuta), 1380-1, Tarazaki, Hitachinaka-shi, Ibaraki, 312-0003, Japan, declare that;

1. I got a Master degree in science from Tsukuba University in 1990, and entered Hitachi Chemical Company, Limited in April 1990. I have made researches in CMP in Hitachi Chemical Company, Limited since October 1995.
2. I am one of the named inventors of the above-identified application and am familiar with the subject matter disclosed in said application.
3. The following additional experiments were conducted to show the unexpected effects achieved by the present invention which cannot be found out from the references.

(1)Additional Experiment 1

(1-1)Preparation of the chemical mechanical polishing agent

Chemical mechanical polishing agents (Chemical A, Chemical B, and Chemical C) were prepared respectively by adding water to materials given below. Here, concentration of the oxidation agent for each agent was varied by changing H_2O_2 in amount. Further, pH was changed by changing the amount of malic acid. Table 1 shows concentration of the oxidation agent and pH for each Chemical A, B and C.

Composition of medium:

BTA 0.2 wt%

MeOH 0.6 wt%

Colloidal silica(24 nm) 1 wt%

H_2O_2 0.15-9 wt%

Malic acid (0)0.005-0.5 wt%

Table 1

| Sort | Chemical A | Chemical B | Chemical C |
|-------------------------|------------|------------|------------|
| pH | 2.5 | 2.2 | 4.0-(6.4) |
| H_2O_2 conc. (wt%) | 0.15 | 9 | 0.15 |

(1-2)Polishing

Using the chemical mechanical polishing agents thus obtained, CMP (Chemical Mechanical Polishing) were carried out under the following polishing conditions.

Substrate:

A silicon substrate on which a tantalum film in thickness 200 nm is formed

A silicon substrate on which a nitrogen tantalum film in thickness 100nm is formed

A silicon substrate on which silicon dioxide film in thickness of 1 μm is formed

A silicon substrate on which a copper film in thickness of 1 μm is formed

Polishing pad:

Foaming polyurethane resin with closed-cell

Polishing pressure: 250 gf/cm²

Relative velocity between the substrate and the polishing platen: 18 m/min

(1-3) Evaluation Item of the polishing products

The following Items were evaluated for each of the polished products having been subjected to CMP.

Polishing speed of CMP:

The difference of the film thickness before and after CMP was obtained through conversion based on a value of electric resistance.

(1-4) Evaluation result

The polishing speeds of CMP thus measured for respective samples are shown in Table 2 and Fig. 1

Only in a case of Chemical A having a liquid composition as claimed in the present invention, namely, a low pH and a low concentration of the oxidation agent, even in a liquid composition containing 1 wt% of minute colloidal silica, a high speed polishing of the Ta base film is achieved while controlling the polishing speed of the Cu film.

For Chemical B, which has the same liquid composition as Chemical A, but has a higher concentration of oxidation agent than Chemical A, the polishing speed of the Ta base film has decreased and the polishing speed of the Cu film has increased by a large amount. Its pH has slightly decreased (2.5 → 2.2) due to the increase of the H_2O_2 concentration.

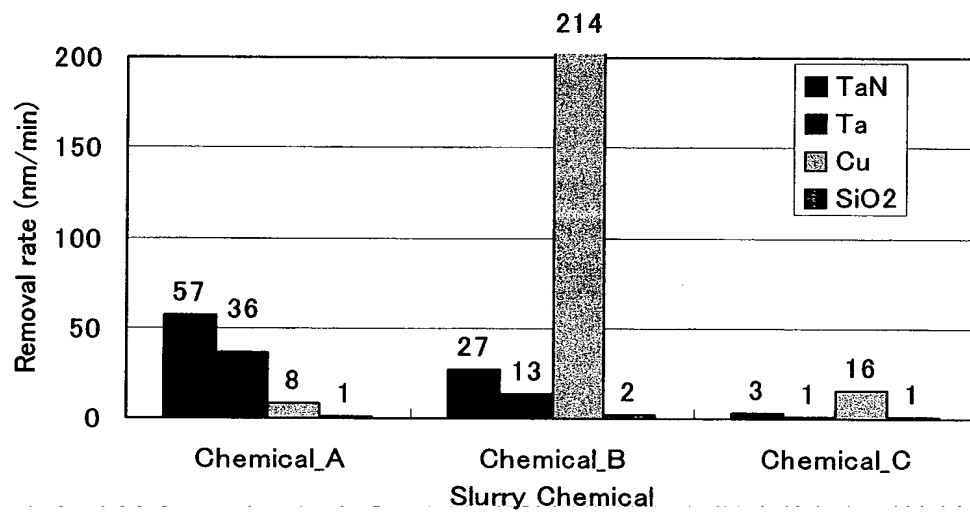
Further for Chemical C, which has the same liquid composition as Chemical A having the same concentration of the oxidation agent, but has pH 4 or higher which has been adjusted only by reducing the concentration of malic acid, the polishing speed of the Ta base film is hardly obtained.

That is, the liquid composition having a low pH and a low concentration of the oxidation agent shows specific properties which achieve a high-speed polishing of the Ta base film with a slight amount of minute abrasive grains.

Table2

| Film | Chemical A | Chemical B | Chemical C |
|------------------|------------|------------|------------|
| TaN | 57 | 27 | 3 |
| Ta | 36 | 13 | 1 |
| Cu | 8 | 214 | 16 |
| SiO ₂ | 1 | 2 | 1 |

Fig.1



(2) Additional Experiment 2

Chemical mechanical polishing agents, (Chemical A and B) are prepared for the experiment 2 in the same manner as in the additional experiment 1, except that the abrasive sizes of the Chemical A and Chemical B have been changed as shown in Table 3. Evaluation was carried out in the similar manner as the experiment 1. The result is shown in Table 3 and Fig. 2.

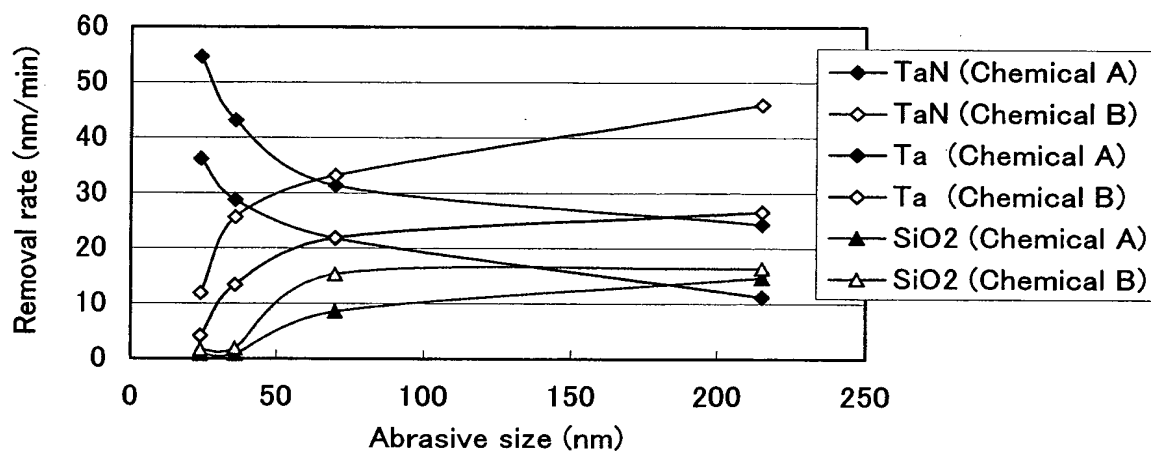
Regarding the dependency on abrasive grain diameter when the concentration of the abrasive grain is fixed to 1 wt%, Chemical B shows a polishing tendency that the general mechanical action is dominant, that is, as for both the Ta base film and the SiO₂ film, the polishing speed gets faster as the abrasive grain diameter gets larger.

In contrast, as for Chemical A being the present invention, the polishing speed of the SiO₂ film shows the similar tendency as that of Chemical B but the polishing speed of the Ta base film shows a specific property that the polishing speed gets faster as the grain diameter gets smaller.

Table3

| Abrasive size (nm) | TaN (Chemical A) | TaN (Chemical B) | Ta (Chemical A) | Ta (Chemical B) | SiO ₂ (Chemical A) | SiO ₂ (Chemical B) |
|--------------------|------------------|------------------|-----------------|-----------------|-------------------------------|-------------------------------|
| 24 | 54.7 | 11.9 | 36.2 | 4.2 | 0.8 | 1.6 |
| 36 | 43.2 | 25.7 | 28.8 | 13.4 | 0.8 | 1.9 |
| 70 | 31.4 | 33.2 | 21.8 | 21.9 | 8.5 | 15.3 |
| 215 | 24.4 | 46 | 11.2 | 26.6 | 14.7 | 16.4 |

Fig.2



(3) Additional Experiment 3

Chemical mechanical polishing agent was prepared by adding water in materials shown below. Here, pH was varied by changing the amount of malic acid as shown in Table 4. Evaluation was carried out in the similar manner as the Experiment 1. The result is shown in Table 4 and Fig. 3.

Regarding the dependency on pH of a slurry in a composition of a low H_2O_2 concentration of 0.15 wt%, when pH is 4 or larger, the Ta base film is hardly polished. A high speed polishing speed is stably obtainable when pH is under 3 as the present invention.

On the other hand, polishing speeds of the Cu film and the TiN film show behaviors completely different from that of the Ta base film. In this slurry composition containing 1wt % of minute colloidal silica, a force of mechanical action is very small, and therefore, the SiO_2 film is hardly polished regardless of its pH.

Composition of polishing medium:

BTA 0.2 wt%

MeOH 0.6 wt%

Colloidal silica(36nm) 1 wt%

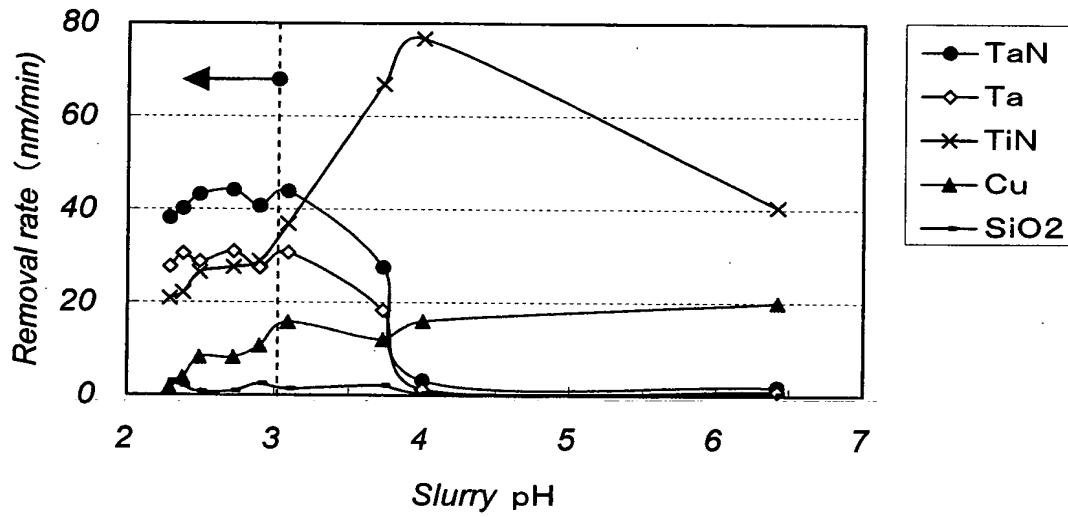
H_2O_2 0.15 wt%

Malic acid 0-1.2 wt%

Table 4

| Malic acid conc.(wt%) | pH | TaN | Ta | TiN | Cu | SiO ₂ |
|-----------------------|------|------|------|------|------|------------------|
| 0 | 6.42 | 1.9 | 0.9 | 40.5 | 20.0 | 0.4 |
| 0.005 | 4.00 | 3.2 | 1.3 | 76.7 | 16.0 | 0.4 |
| 0.01 | 3.73 | 27.6 | 18.3 | 66.9 | 12.0 | 2.1 |
| 0.05 | 3.09 | 43.9 | 30.7 | 36.9 | 15.8 | 1.4 |
| 0.1 | 2.90 | 40.8 | 27.5 | 28.9 | 10.6 | 2.5 |
| 0.2 | 2.72 | 44.2 | 31.0 | 27.6 | 8.2 | 0.9 |
| 0.5 | 2.49 | 43.2 | 28.8 | 26.5 | 8.2 | 0.8 |
| 0.8 | 2.38 | 40.2 | 30.5 | 22.1 | 3.7 | 2.0 |
| 1.2 | 2.29 | 38.2 | 27.7 | 20.9 | 1.6 | 3.0 |

Fig. 3



(4) Additional experiment4

Chemical mechanical polishing agent was prepared by adding water in materials shown below. Here, concentration of the oxidation agent was changed by changing H_2O_2 in amount as shown in table 5. Further, Table 5 shows pH of the respective polishing agents. Evaluation was carried out in the similar manner as the Experiment 1 and the result is shown in table 5 and Fig. 4.

Regarding the dependency on concentration of oxidation agent in slurry prepared based on the original slurry of about 2.5 pH, it shows a tendency that the polishing speed of the Ta base film gradually decreases as the concentration of H_2O_2 increases.

In contrast, the polishing speed of the Cu film and the TiN film inversely does increases in conjunction with increase of the concentration of H_2O_2 . In particular, polishing speed of the Cu film is considerably high when the H_2O_2 concentration is more than 3 wt% compared to the polishing speed of the Ta base film. When a Ta base barrier film with Cu wirings is polished with slurry having such a polishing speed ratio, there arises a problem of dishing increase. Therefore it is preferable that the H_2O_2 concentration is kept 3 wt% or lower. In this slurry composition containing 1 wt% of minute colloidal silica, a force of mechanical action is small, and therefore, the SiO_2 film is hardly polished regardless of the concentration of the oxidation agent.

In this experiment, pH of the slurry shows a tendency to slightly decrease because of the increase of the H_2O_2 concentration, but it remains within a range of 2.5-2.2.

Composition of polishing medium:

BTA 0.2 wt%

MeOH 0.6 wt%

Colloidal silica(36nm) 1 wt%

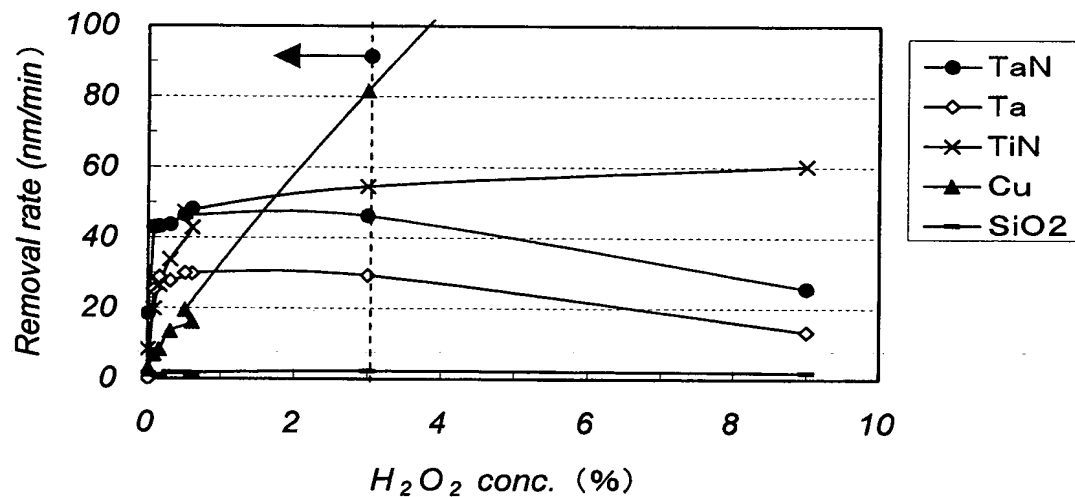
H_2O_2 0.9 wt%

Malic acid 0.5 wt%

Table 5

| H ₂ O ₂ conc.(wt%) | TaN | Ta | TiN | Cu | SiO ₂ | pH |
|---|------|------|------|-------|------------------|------|
| 0 | 18.5 | — | 8.3 | 3.0 | 1.5 | 2.47 |
| 0.075 | 43.0 | 25.3 | 19.8 | 6.8 | 0.9 | 2.49 |
| 0.15 | 43.2 | 28.8 | 26.5 | 8.2 | 0.8 | 2.49 |
| 0.3 | 43.7 | 27.8 | 33.8 | 13.4 | 1.7 | 2.49 |
| 0.6 | 48.2 | 29.8 | 42.9 | 16.1 | 1.0 | 2.48 |
| 0.5 | 46.4 | 30.0 | 47.3 | 19.5 | 1.7 | 2.45 |
| 3 | 46.3 | 29.4 | 54.6 | 81.7 | 2.3 | 2.41 |
| 9 | 25.7 | 13.4 | 60.4 | 213.5 | 1.9 | 2.22 |

Fig.4



(5) Additional Experiment 5

Chemical mechanical polishing agent was prepared by adding water in materials shown below. Here, concentration of the oxidation agent was changed by changing H_2O_2 in amount as shown in Table 6. Further, Table 5 shows pH of the respective polishing agents. Evaluation was carried out in the similar manner as the experiment 1. Table 6 and Fig. 5 show the Evaluation result.

Regarding the dependency on a concentration of oxidation agent containing PAA(Polyacrylic acid ammonium salt) as a water-soluble polymer, prepared based on an original slurry of about pH 2.8, it shows a tendency that the polishing speed of the Ta base film decreases as the concentration of H_2O_2 increases. Compared to the result of the additional Experiment 4, the decrease in the polishing speed with respect to the increase of the H_2O_2 concentration is noticeable.

On the other hand, polishing speeds of the Cu film and the TiN film, inversely to the Ta base film, increases in conjunction with the increase of the H_2O_2 concentration, in the same manner as the result of the additional Experiment 4. Compared to the result of the additional Experiment 4, the increase of the polishing speeds with respect to the increase of the H_2O_2 concentration is quite noticeable.

Thus, the polishing speed of the Cu film becomes remarkably higher than that of the Ta base film when the H_2O_2 concentration is 1.8 wt% or larger. When the Ta base barrier film with Cu wirings is polished with slurry having such a polishing speed ratio, there arises a problem of dishing increase. Therefore it is preferable that the H_2O_2 concentration is kept 1.8 wt% or lower.

In this slurry composition containing 1 wt% of minute colloidal silica, a force of mechanical action is small, and therefore, the SiO_2 film is hardly polished regardless of the concentration of the oxidation agent. In this experiment, the slurry pH shows a tendency to slightly decrease because of the increase of the H_2O_2 concentration, but it remains within a range of 2.8-2.5.

Composition of polishing medium:

PAA 0.05 wt%

BTA 0.2 wt%

MeOH 0.6 wt%

Colloidal silica(36nm) 1 wt%

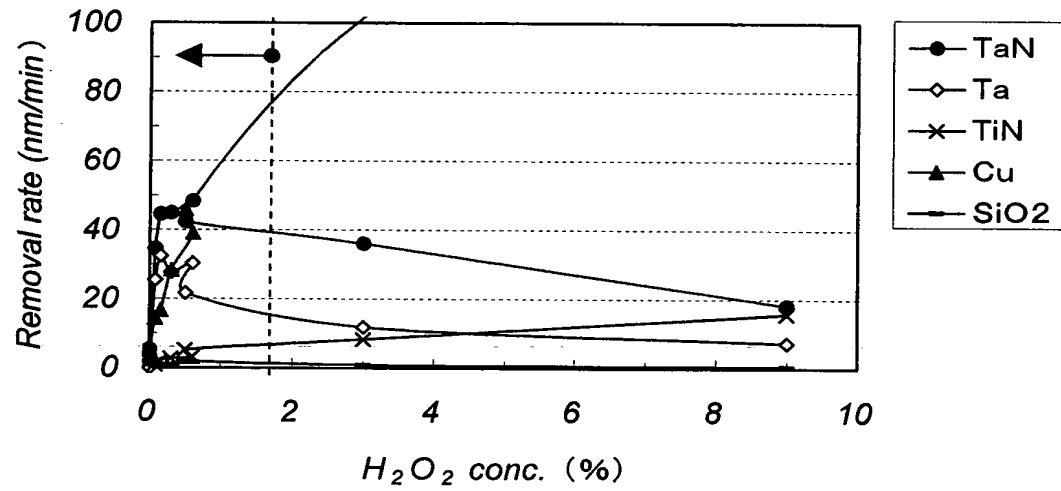
H_2O_2 0.9 wt%

Malic acid 0.5 wt%

Table 6

| H ₂ O ₂ conc.(wt%) | TaN | Ta | TiN | Cu | SiO ₂ | pH |
|---|------|------|------|-------|------------------|------|
| 0 | 5.4 | — | 1.8 | 4.9 | 1.7 | 2.79 |
| 0.075 | 34.6 | 25.5 | 0.9 | 14.4 | 0.7 | 2.78 |
| 0.15 | 44.6 | 32.5 | 1.9 | 16.7 | 0.7 | 2.77 |
| 0.3 | 44.9 | 27.8 | 2.7 | 28.4 | 0.9 | 2.79 |
| 0.6 | 48.4 | 30.4 | 3.1 | 39.1 | 1.6 | 2.74 |
| 0.5 | 42.4 | 21.7 | 5.2 | 46.0 | 1.9 | 2.72 |
| 3 | 36.1 | 11.9 | 8.3 | 101.8 | 0.9 | 2.71 |
| 9 | 18.3 | 7.4 | 15.8 | 179.1 | 0.5 | 2.51 |

Fig.5



(6) Additional Experiment 6

Chemical mechanical polishing agent was prepared by adding water in materials shown below. Here, pH of the respective polishing agent was changed by changing the amount of malic acid as shown in Table 7. Evaluation was carried out in the similar manner as the experiment 1. The result is shown in Table 7 and Fig. 6.

Regarding the dependency on pH of slurry containing PAA (Polyacrylic acid ammonium salt) as a water-soluble polymer, having a low H_2O_2 concentration of 0.15 wt%, when pH is 4 or larger, the Ta base film is hardly polished. A high polishing speed is stably obtainable when pH is below 3 as the present invention.

On the other hand, polishing speeds of the Cu film and the TiN film show behaviors completely different from that of the Ta base film. In this slurry composition containing 1 wt % of minute colloidal silica, a force of mechanical action is small, and therefore, the SiO_2 film is hardly polished regardless of the pH.

Composition of polishing medium:

PAA 0.05 wt%

BTA 0.2 wt%

MeOH 0.6 wt%

Colloidal silica(36nm) 1wt %

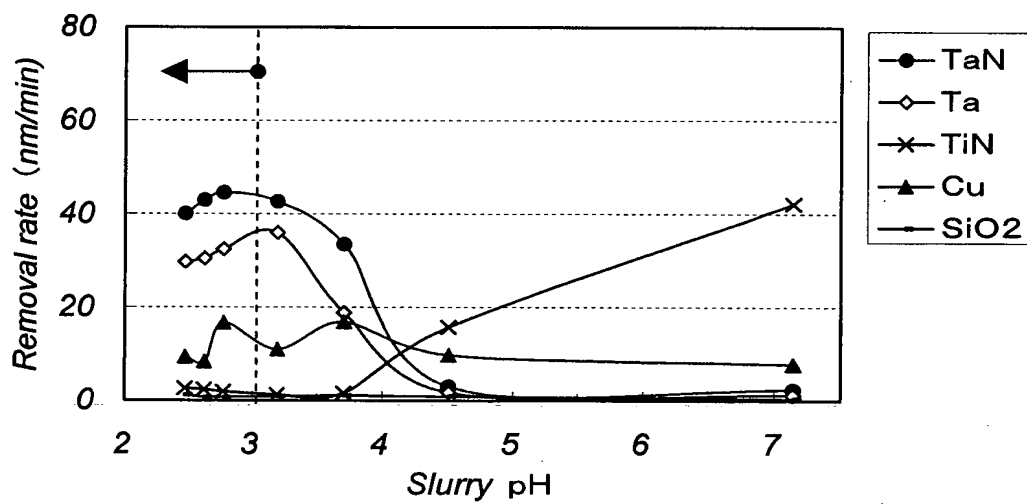
H_2O_2 0.15 wt%

Malic acid 0-1.2 wt%

Table 7

| Malic acid conc.(wt%) | pH | TaN | Ta | TiN | Cu | SiO ₂ |
|-----------------------|------|------|------|------|------|------------------|
| 0 | 7.14 | 2.4 | 1.2 | 42.2 | 7.8 | 0.4 |
| 0.05 | 4.51 | 3.1 | 1.8 | 15.8 | 9.8 | 0.9 |
| 0.1 | 3.71 | 33.6 | 18.9 | 1.6 | 16.9 | 1.1 |
| 0.2 | 3.19 | 42.7 | 36.0 | 1.3 | 11.0 | 0.9 |
| 0.5 | 2.77 | 44.6 | 32.5 | 1.9 | 16.7 | 0.7 |
| 0.8 | 2.62 | 43.0 | 30.5 | 2.4 | 8.4 | 0.7 |
| 1.2 | 2.47 | 40.1 | 29.8 | 2.6 | 9.4 | 1.2 |

Fig.6



The undersigned DECLARANT declares further the all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that the willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Execute this 26 th day of May , 2005.

Yasushi Kurata
Yasushi Kurata